

1 **AN IMPROVED SCALABLE METHOD OF ISOLATING**
2 **ASPHALTENES.**

3 Maksymilian Plata-Gryl¹, Christian Jungnickel², Grzegorz Boczkaj^{1,*}

4 ¹Gdansk University of Technology, Faculty of Chemistry, ¹Department of Chemical and
5 Process Engineering,

6 ² Gdansk University of Technology, Faculty of Chemistry, Department of Colloid and
7 Lipid Science.

8 * *Dr Grzegorz Boczkaj, PhD. Sc. Eng. Gdansk University of Technology, Faculty of*
9 *Chemistry, Department of Chemical and Process Engineering, 80 – 233 Gdansk, G.*
10 *Narutowicza St. 11/12, Poland. Fax: (+48 58) 347-26-94; Tel: (+48) 697970303; E-mail:*
11 grzegorz.boczkaj@gmail.com

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15 **ABSTRACT**

16 A new, improved and scalable procedure of asphaltene fraction isolation is presented and
17 compared to standard test methods. The new procedure uses 1:40 feedstock to solvent (n-
18 heptane) ratio (g/mL), filtration through a cellulosic thimble and extensive washing in a
19 Soxhlet type extractor. The group type composition and purity of the asphaltene fractions
20 have been examined using thin-layer chromatography with flame-ionization detection. This
21 study revealed that the new procedure provides a higher purity of asphaltene fraction
22 resulting in a more accurate determination of its content in bitumens when comparing to the
23 standard test method. Moreover, an attempt of evaluation of the scale-up possibility of the
24 proposed and standard test methods was made, revealing that new procedure is more
25 scalable than standard test methods. It is possible to obtain large quantities of a high purity
26 asphaltene fraction even on a process scale. This feature is crucial for technical analytics, for
27 researchers studying asphaltene characteristic as well as for other novel applications of
28 asphaltene such as its use as sorbents in separation techniques.

29

30 1. Introduction

31 Asphaltenes are the most aromatic group of chemical compounds present in the
32 crude oil and the heaviest products of its processing; they quantitatively remain in a residue
33 from vacuum distillation. Due to their complex composition, asphaltenes are a class of
34 compounds defined on the basis of solubility (Linton, 1894; Marcusson, 1911; Parr et al.,
35 1909) rather than molecular structure. They are insoluble in n-alkanes e.g. n-heptane, and
36 soluble in toluene or benzene (Ferris et al., 1967; Hubbard and Stanfield, 1948;
37 Kleinschmidt, 1955; Mitchell and Speight, 1973; O'Donnell et al., 1951; Strieter, 1941). In
38 terms of molecular structure, asphaltenes are polycyclic aromatic compounds (PACs)
39 comprised of 4-10 fused aromatic rings, peripherally attached alkyl chains and polar
40 functional groups e.g. carboxylic acids, phenol, and pyridines (Groenzin and Mullins, 2000;
41 Mullins, 2011, 2010). They consist mostly of hydrogen and carbon, with H:C ratio of about 1-
42 1.2, and additionally heteroatoms such as oxygen, sulfur, nitrogen and trace amounts of
43 vanadium and nickel can be found in their backbone (Leyva et al., 2013; Trejo et al., 2004).
44 Typical asphaltene molecules have an average molecular weight of 750 g/mole (Badre et al.,
45 2006; Groenzin and Mullins, 2000; Pomerantz et al., 2015) and are arranged into planar type
46 structures with a tendency to form nanoaggregates (about six asphaltene molecules) and
47 clusters (about eight nanoaggregates) (Mullins, 2010; Pomerantz et al., 2015; Schuler et al.,
48 2015).

49 Asphaltenes exhibit wide range of interactions e.g. van der Waals, Coulombic,
50 hydrogen bonding, and π - π stacking (Murgich, 2002). Because of their physicochemical
51 similarity to resins, asphaltenes exhibit strong sorption interactions with them. In solution,
52 asphaltene-resin interactions can be favoured over asphaltene-asphaltene interactions
53 (Speight, 2004). Resins can adsorb in the form of multilayers on the surface of the
54 asphaltenes and penetrate their microporous structure (León et al., 2002; Liao et al., 2005).
55 This is beneficial when considering stability of refinery process streams, as resins stabilize

56 asphaltenes in colloidal form (Aguilar and Mansur, 2015; Andersen and Speight, 2001; Koots
57 and Speight, 1975), but can be a drawback if the purpose is to isolate pure asphaltenes.

58 Asphaltenes are of crucial importance in the petroleum industry, mainly due to the
59 several technological issues created by them in crude oil processing *i.e.* formation of
60 emulsions, fouling, well-bore and pipelines clogging, coke formation, and catalyst
61 deactivation in conversion processes (Akbarzadeh et al., 2007; Almehaideb, 2004; Idris and
62 Okoro, 2013; Kokal and Sayegh, 1995; Ramirez-Jaramillo et al., 2006). Currently,
63 asphaltenes are utilized only in the production of bitumens, bitumen mixtures and mineral
64 rubber (Rostler and Sternberg, 1949). Their content in bitumen is increased by oxidation (air
65 blowing process) (Moschopedis and Speight, 1975) for upgrading of primary properties of
66 vacuum residue, measured by penetration, softening point and breaking point parameters.
67 They describe the stiffness and behavior of bitumen in high and low temperatures of its
68 usage.

69 Recently, Boczkaj et. al. (2016) showed that asphaltenes present the possibility of
70 being applied as a sorbent in separation techniques. Their unique selectivity, high thermal
71 stability and low production cost makes it an interesting material for stationary phases for gas
72 chromatography, as well as for preparative and process separations (Boczkaj et al., 2016,
73 2015). However, current methods of isolation are not sufficient for providing large scale
74 quantities of this material. Therefore a new method is required.

75 Traditionally, asphaltenes are isolated by means of precipitation with saturated
76 hydrocarbons, such as *n*-pentane and *n*-heptane (ASTM D2007, 2003; ASTM D3279, 2001;
77 ASTM D4124, 2001; ASTM D6560, 2000). Precipitation conditions *i.e.* type of solvent type,
78 solvent to feedstock ratio, standing time and temperature have a significant impact on the
79 yield of obtained asphaltenes and co-precipitated resins (Andersen and Birdi, 1990; H.
80 Alboudwarej et al., 2002; Mitchell and Speight, 1973; Speight et al., 1984). Thus, asphaltene
81 fractions isolated under different conditions are not identical and consequently have different
82 properties. Although some groups indicate that the mechanism of precipitation is
83 independent of the isolation method, but rather that the quantity of isolated asphaltenes is of



84 the same magnitude, their characteristic should also be the same (Andersen and Birdi,
85 1990).

86 The type of solvent and its amount have the most evident effect on the precipitate.
87 The yield of asphaltenes increases with increasing number of carbons in an n-alkane and
88 reaches a plateau using n-heptane. The usage of n-heptane as a solvent is favoured when
89 asphaltenes are the subject of research, because their properties are virtually stable for n-
90 alkanes above n-hexane (Andersen and Birdi, 1990; H. Alboudwarej et al., 2002; Mitchell
91 and Speight, 1973; Speight et al., 1984). Studies revealed that to provide efficient separation
92 of asphaltenes, at least 30mL of solvent to each gram of feedstock is necessary (H.
93 Alboudwarej et al., 2002; Speight et al., 1984). Although settling time can have a significant
94 impact on the obtained asphaltene fraction purity, it varies considerably in standard test
95 methods; from 30 minutes (ASTM D2007, 2003) up to 16 hours (ASTM D4124, 2001).
96 Studies revealed that to ensure stable yields of asphaltenes, standing time of about 8-10h is
97 needed. Extending this time above 16h may lead to the adsorption of resins from the liquid
98 on the asphaltenes surface (Speight et al., 1984).

99 A number of studies investigated the effect of temperature on asphaltenes
100 precipitation. However in this case, conflicting information emerges, with some report a
101 decrease in asphaltenes yield with increasing temperature (Ali and Al-Ghannam, 1981;
102 Mitchell and Speight, 1973) and the possibility of enhanced co-precipitation of resins
103 (Speight et al., 1984), while others indicate increased yield in higher temperatures
104 (Andersen, 1994; Andersen and Birdi, 1990; Hu and Guo, 2001). Andersen and Birdi (1990)
105 observed an increased yield of precipitate followed by decrease after reaching maximum at
106 25 °C. He ascribed it to enhanced adsorption of smaller molecules and further rupture of
107 those interactions (desorption of molecules) as the temperature increases further. However,
108 the most recent studies seem to confirm a decrease in yield of asphaltenes with increasing
109 temperature (Andersen, 1995, 1994, Andersen et al., 1998, 1997; Andersen and Stenby,
110 1996; Hu and Guo, 2001; Maqbool et al., 2011) and a lower content of resins when
111 precipitation is carried out at higher temperatures (Pineda et al., 2007). UV fluorescence



112 studies revealed that when temperature decreases more compounds with smaller fused rings
113 precipitate. Conversely, when the precipitation temperature increases, the isolated fraction is
114 dominated by larger aromatic structures (Andersen and Birdi, 1990). This result is supported
115 by molecular weight studies, as molecular mass increase when asphaltenes are precipitated
116 at elevated temperatures. Another consequence of increased precipitation temperature is
117 higher aromaticity (*i.e.* lower H/C ratio) and polarity of isolated fraction (Andersen, 1995,
118 1994; Andersen et al., 1997; Pineda et al., 2007). In the scope of the definition and up-to-
119 date structural information about asphaltenes, as well as being insoluble in n-alkanes and
120 consisting of aromatic core of 4-10 fused rings, the variation of temperature affects the
121 precipitate yield due to the co-precipitation of smaller molecules (e.g. resins). Although, one
122 need to remember that there is no distinct border between asphaltenes and resins.

123 The last step of almost all precipitation procedures include washing of the isolated
124 asphaltenes, is to remove adsorbed resins as well as other components of the primary
125 material (ASTM D2007, 2003; ASTM D3279, 2001; ASTM D4124, 2001; ASTM D6560,
126 2000). If asphaltenes-resins interactions are adsorptive, then it should be possible to remove
127 resins with re-precipitations and/or intensive washing with the correct solvent. The second
128 phenomenon that can hinder the isolation of pure asphaltenes is to block access of the
129 solvent by occlusion, thus retaining resins (or generally other than asphaltene fractions) by
130 asphaltenes (Derakhshesh et al., 2013; Liao et al., 2006, 2005; Strausz et al., 2006).
131 Although, the importance of the washing step is recognised intuitively, it is the most
132 imprecise and ambiguous step. Usually it is performed on a filter with the solvent used for the
133 precipitation. A common criterion is to continue washing until the effluent is colourless (ASTM
134 D4124, 2001). This implies arbitrariness and leads to different extents of washing. Another
135 popular method of washing is to use a reflux extractor (ASTM D6560, 2000). Results
136 presented in (H. Alboudwarej et al., 2002) revealed that using Soxhlet's extractor led to
137 removal of 22% w/w of maltenes from filter-washed asphaltenes.

138 As we have shown, a number of methods and refinements exist to isolate
139 asphaltenes, but none allow for large scale production of a consistently pure product.



140 Therefore, the aim of this paper was to propose simplified, reproducible, easy to scale – up
141 procedure of asphaltenes isolation, which will give at least similar results as the standard test
142 method. It would be of great importance, not only for studies in our research group (Boczkaj
143 et al., 2016), but for researchers studying asphaltenes characteristic and technical analysis
144 of petroleum products as well. Usually asphaltenes are characterized by their average
145 properties e.g. elemental composition and molar mass. In this paper, thin-layer
146 chromatography with flame ionization detection (TLC-FID) was used to compare group type
147 composition of asphaltene fractions obtained by studied methods. Moreover operation
148 effectiveness, scale-up possibility as well as economic aspects of this methods were
149 evaluated.

150 **2. Experimental**

151 **2.1. Materials**

152 Bitumen 20/30 SDA (Lotos Group, Gdansk, Poland) and n-heptane EMPLURA®
153 (Merck, Germany) were used to isolate the asphaltene fraction. Depending on the isolation
154 method used, mixture was filtered through a 0.45µm PTFE membrane filter (Achrom,
155 Belgium) or a standard single thickness 33x100mm cellulose thimble (VWR, United States).
156 During hydrocarbon group type analysis of the isolated fractions, the following analytical
157 grade chemicals were used: dichloromethane (POCH, Poland), methanol (POCH, Poland),
158 toluene (POCH, Poland) and hexane (Merck, Germany). To filter samples prior to analysis,
159 0.45µm PTFE syringe filters (Achrom, Belgium) were used.

160 **2.2. Apparatus**

161 To perform filtration a vacuum glass set (Glassco, India) was used. Isolated samples
162 were washed in a Soxhlet type extractor. Weight measurements were performed with a WLC
163 6/A2 (readability 0.1g) and WPA 180/C (readability 0.1mg) balances (RADWAG, Poland).

164 To analyze the group type composition of the isolated fractions by means of TLC-FID
165 technique an Iatroscan Mk.V (Iatron Lab., Japan), silica gel Chromarods S5 (Iatron Lab.,

166 Japan), 3200/IS-01 semiautomatic sampler (SES, Germany), 7102KH 2 μ L syringe (Hamilton,
167 USA), TLC TK-8 Chromarods dryer (Iatron Lab., Japan), chromatographic chambers, AD
168 converter, and corresponding software (Chomik, Poland) were used.

169 **2.3. Procedures**

170 **2.3.1. Asphaltene fractions isolation**

171 **2.3.1.1. Procedure ASTM D4124**

172 The reference samples of asphaltene fraction were isolated using the conditions
173 described in ASTM D4124 (ASTM D4124, 2001). As a reference standard method of
174 isolation ASTM D4124 was selected, because it exploits high solvent to feedstock ratio
175 (100mL : 1g), long contact time (ca.16h) and extensive washing of isolated asphaltenes (till
176 effluent is colorless). This should ensure high purity (low content of resins) of the asphaltene
177 fraction. Bitumen was heated in an oven at 70°C for 1h and 6g (weighed to the nearest 0.1g)
178 were placed in 1L flask, which was gently heated to disperse bitumen on the bottom and
179 lower sides of the flask. Next, the n-heptane was added in the ratio of 100mL per 1g of
180 bitumen. The mixture was heated to boiling and refluxed for 1h with occasionally stirring.
181 After the mixture was allowed to cool for 16h, it was filtered through 0.45 μ m PTFE
182 membrane filter under the vacuum. The precipitate was washed with hot n-heptane until a
183 colorless filtrate was obtained. The filtrate was consequently washed with 80mL of fresh n-
184 heptane, and heated for 30min with occasional stirring and filtered again through a fresh
185 tared PTFE membrane filter. The asphaltene cake was washed with hot n-heptane till the
186 filtrate was colorless, dried (1h at 100°C) and weighed.

187 **2.3.1.2. Procedure B1 and B16**

188 The novel procedure of isolation proposed and tested in this paper is as follows:
189 bitumen is heated in an oven at 70°C for 1h and 15g of it is placed in 1L round-bottom flask.
190 The flask is gently heated to disperse bitumen on the bottom and lower sides of the flask.
191 Next, the n-heptane is added in the ratio of 40mL per 1g of the bitumen. The mixture is
192 brought to a boil and refluxed for 1h with occasional stirring. Then it is set aside for 1h

193 (procedure B1) and 16h (procedure B16) to cool and the content of the flask is filtered
194 through a tared cellulose thimble. In procedure B1 the filtration started at temperature of the
195 mixture being 55 °C, and in B16 procedure at 20 °C. The thimble is placed in a Soxhlet
196 extractor and washed with n-heptane for 24h. Next, it is dried at 100°C for 1h and weighed.

197 Figure 1 and 2 present steps of standard and proposed procedures for isolation of
198 asphaltene fraction and experimental glassware setup, respectively.

199 **2.3.2. Hydrocarbon group type analysis of isolated fractions.**

200 The group type composition of bitumen and the isolated fractions was investigated by
201 TLC-FID technique which allows a relatively fast analysis. A normal phase separation
202 mechanism is used, resulting in a so-called SARA (Saturates, Aromatics, Resins,
203 Asphaltenes) analysis. In this conditions asphaltenes are defined as a group of compounds
204 having the highest retention.

205 Samples were prepared by dissolving the samples in dichloromethane to yield
206 concentration of 2 mg/mL. This prevents overloading of the stationary phase and leads to a
207 better separation of asphaltenes and resins. To remove any undissolved particles, the
208 samples were filtered through 0.45µm PTFE syringe filters. Before spotting the samples, the
209 Chromarods were activated in the flame of FID detector: once in time of 35s and twice in
210 50s. Then, they were placed in desiccator for 10min to cool down.

211 1µL of the samples were spotted in a small aliquots on the three Chromarods each, to
212 obtain quantitative results. Next, the Chromarods with the spotted samples were placed in
213 the dryer (set to 70°C) for 3min. A three-step elution sequence was used, with eluents in the
214 following order:

- 215 1. dichloromethane:methanol (95:5 v/v) elution up to 45% of a stationary phase height
- 216 2. toluene elution up to 80% of a stationary phase height
- 217 3. n-hexane (95% water saturated) elution up to 100% of a stationary phase height

218 The set of solvents used in this work is a typical set used for hydrocarbons group type
219 analysis of petroleum heavy fractions using TLC-FID technique (Sharma et al., 1998).

220 However, atypical is the sequence of the elution, which is contrary to what can be typically
221 found in literature (Jiang et al., 2008; Sharma et al., 1998). In our work we developed the
222 Chromarods beginning with the solvent ensuring the elution of asphaltene fraction. It follows
223 from the high amount of asphaltene in the sample which are not solubilized and eluted by n-
224 hexane (which is used as the first solvent in typical procedures). In our opinion fractions
225 other than asphaltenes (i.e. saturates and aromatics) can be trapped under asphaltenes and
226 shielded/covered by them, hence not eluted by the n-hexane used as first solvent. First
227 solvent (dichloromethane:methanol) eluted all components of the spotted sample and
228 increased accessibility of two other solvents to the whole amount of the sample. This
229 approach was validated in our lab during a series of quality control analysis of bitumen,
230 performed for a local refinery in Gdansk.

231 Each TLC chamber was lined with chromatographic paper, filled with eluent and left for
232 saturation for 15min. The Chromarods were placed in the chamber and eluted accordingly.
233 Before elution with toluene and n-hexane the frame with rods was held in headspace of
234 eluent for 5 min to saturate the stationary phase with vapors of the eluent. After each elution
235 step the rods were dried for 3min (or longer if a scent of a solvent was noticeable) and left in
236 desiccator for 10 min to cool down.

237 Detection was carried out in a TLC-FID analyzer. Rod scanning time was set to 35s,
238 hydrogen and air flow were 150mL/min and 1800mL/min respectively. Chromatograms were
239 integrated with a normalization method. Obtained results were used comparatively for
240 evaluation of purity of asphaltene fraction obtained by means of studied in this paper
241 methods of isolation.

242 **2.4. Quality assurance of data.**

243 The average results for isolation of asphaltene fraction, by each procedure, are the mean
244 values of three separate isolations. The average yield is a mass ratio of asphaltene fraction
245 and feedstock (bitumen). For TLC-FID analysis, each sample was spotted on three rods to
246 provide quantitative data. The average of asphaltenes content was calculated as a mean of



247 the means for individual samples isolated with given procedure. The relative standard
248 deviation (RSD%), which expresses the precision and repeatability was calculated as a ratio
249 of standard deviation to the mean value of asphaltenes content, multiplied by one hundred.

250 To compare the accuracy of investigated procedures, mean results (which were obtained
251 by the same analyst) were evaluated by means of F-Snedecor test, to confirm the
252 homogeneity of variances and next with t-Student test. t-Student test is used for determining
253 whether the observed difference between obtained means is statistically significant or not. F-
254 Snedecor test is performed to check whether the variances of the two samples are equal and
255 if t-Student test without correction can be used.

256 3. Results and discussion

257 Figure 3 shows exemplary TLC-FID chromatograms (SARA analysis) of analyzed
258 sample isolated by B1 (B) procedure and feedstock bitumen (A). A baseline separation
259 between resins and asphaltenes is obtained, allowing to control the precipitation.

260 Table 1 presents results of TLC-FID analysis of obtained asphaltene fractions. Table
261 2 presents differences between values of parameters given in Table 1 for the tested
262 procedures.

263 Isolated asphaltene fractions were dark brown, black mat solids. Quantitative analysis
264 revealed some differences which are consistent with obtained yields of asphaltene fractions.
265 It is clear from data in Table 1 that ASTM standard test method has a false positive error i.e.
266 it reports higher content of asphaltenes in bitumen due to the presence of impurities of resins
267 fraction co-precipitating or adsorbing on asphaltenes. The studied alternative procedures
268 exhibit an improved purity of obtained asphaltene fraction. It is possible, that in the case of
269 bitumens having lower content of asphaltenes and higher of resins, this error for ASTM
270 methods would be higher.

271 The average result of asphaltene fraction yield was 10.14 % w/w from the ASTM
272 D4124 procedure and 8.79 % w/w from the new B1 procedure. This difference is mainly the
273 result of lower resins content when proposed B1 procedure is used. These conclusions are



274 supported by the TLC-FID data, which revealed that the asphaltenes content in isolated
275 fraction is higher by 1.59% for B1 procedure.

276 The lowest yield of asphaltene fraction was obtained for our procedure with B1
277 contact time. At the same time this procedure gave the highest purity of asphaltenes. This
278 indicates that B1 procedure, involving the washing in the Soxhlet, washed out more maltenes
279 than the ASTM D4124, in which washing of the filter cake is performed manually.
280 Additionally, the developed procedures have improved reproducibility, as the RSD% value is
281 lower, comparing with ASTM method.

282 The second variant of the procedure, in which contact time was the same as in ASTM
283 D4124 method, gave the results between standard and B1 procedures. The yield of
284 asphaltene fraction was higher and purity of asphaltenes lower than in B1 procedure.
285 Probably, it is due to a lower temperature of a mixture at the beginning of filtration and
286 resulting higher adsorption of resins in B16 procedure. Still, this method provided higher
287 purity of asphaltenes than ASTM method. This result clearly indicates the problem of the
288 presence of resins fractions in precipitated asphaltenes fraction, which is almost completely
289 solved in the developed method for optimized conditions of settling the solution, filtration and
290 Soxhlet extraction stages.

291 The precision and repeatability of each procedure was sufficient and comparable, as
292 the RSD% value was below 5% (Table 1). Table 3 presents values of calculated and critical
293 parameters for the t-Student and F-Snedecor test. The t-Student test revealed statistical
294 difference between mean results for ASTM D4124 and proposed B1 procedure. No statistical
295 difference was observed for B16 and ASTM D4124 method. Between B16 and B1
296 procedures difference in purity of asphaltene fraction was insignificant, while difference in
297 yield of asphaltene fraction was slightly significant. Comparison of standard deviations
298 revealed that both proposed methods were slightly more precise than the standard test
299 method.

300 As abovementioned, the goal of this research was to develop simple, cost-effective
301 and easy to scale-up procedure of asphaltenes isolation which will give at least similar



302 results, in terms of asphaltene purity, as standard test method. This has been achieved by
303 lowering the feedstock to solvent ratio from 1g per 100mL to 1g per 40mL (this ratio is
304 reported in some of ASTM methods as allowable) along with modification of purification step.
305 As shown in Table 4 solvent consumption in B1 procedure was calculated as three times
306 lower than in ASTM D4124. For ASTM D4124 calculation has been made on the basis of the
307 amount of the solvent used in abovementioned experiment, while for the other two standard
308 test methods quantities of solvent and feedstock specified in standard test method were
309 used.

310 The studies revealed, that washing step is crucial for final asphaltene purity. Lower
311 solvent consumption allowed the use of bigger quantities of feedstock without fall-off in
312 asphaltene fraction purity (in fact, a higher purity was obtained). This may be not only
313 important for process scale isolation, but also in terms of asphaltene research. Due to the
314 high complexity of petroleum and its subfractions, asphaltene are still relatively unknown
315 and poorly studied group of chemical compounds. One of the difficulties associated with the
316 correct characterization of asphaltene is the lack of one universal and standardized method
317 of isolation. Different research teams isolate asphaltene by means of different ASTM or
318 other standard methods described in the literature or perform isolation by means of their own
319 developed procedures. This affects strongly the purity of asphaltene and reproducibility of
320 results, thus making comparisons limited. Proposed simple, reproducible procedure giving
321 high quantities of asphaltene fraction with very low resins content is an important contribution
322 to this issue.

323 Table 4 compares selected parameters of investigated procedures and two additional
324 standard test methods.

325

326 *Time consumption*

327 B1 procedure is the most time consuming but it is caused by the most extensive
328 washing among compared procedures. This extended purification is a must to obtain pure
329 asphaltene fraction and accurate results of determination.

330 In the case of standard test methods the isolation procedure time can be extended by
331 problems with filtration rate. When isolating asphaltene fraction according to ASTM D4124-
332 01, 0.45 μ m PTFE filters were used and especially in the case of higher amounts of
333 asphaltene fraction, the filters have tendency to clog, thus decreasing the rate of filtration and
334 significantly increasing the time of the filtration stage. The same issue may be observed in
335 ASTM D3297 and D6560 procedures which utilize glass filter pads and cellulose quantitative
336 filters, respectively. In B1 procedure filtration under vacuum with sub micrometer filter was
337 replaced with simple filtration through cellulose thimble, in which the washing step is carried
338 out later. No issues with filtration were observed when filtering through thimble and filtrations
339 were completed in time under 15 minutes. To check if no asphaltenes are going through
340 thimble during filtration, effluent was filtered through 0.45 μ m PTFE membrane filter and no
341 solid particles were retained.

342

343 *Solvent consumption, washing and purity of asphaltene fraction*

344 The B1 procedure has the lowest solvent consumption yet the most extensive
345 washing of the isolated fraction, giving the highest purity of asphaltene fraction. ASTM D3279
346 procedure consumes almost three times more solvent than B1 procedure and washing step
347 is very limited. Although there is no data available about purity of asphaltene fraction isolated
348 with ASTM D3279, because it is similar to ASTM D4124, the purity probably will not exceed
349 the one obtained with ASTM D4124.

350 ASTM D6560 uses similar amount of n-heptane but incorporates dissolution/re-
351 precipitation with toluene. It also involves washing in reflux extractor. However, contrary to
352 Soxhlet extractor used in B1 procedure, it is constructed in a way that the solvent is
353 constantly drained from sample. In Soxhlet extractor a chamber is flooded with hot solvent
354 and periodically emptied by siphon. This ensures longer contact time and in case of bigger
355 sample the whole asphaltene fraction should be evenly washed. ASTM D6560 procedure is
356 somewhat alike to B1 in terms of solvent consumption and washing and can yield asphaltene
357 fractions of similar purity.



358

359 *Arbitrariness and laboriousness*

360 Filtration in thimble and further Soxhlet washing allowed to omit a part of ASTM
361 D4124 test method in which filter cake is transferred to beaker for extra washing and avoid
362 manual washing of filter cake, which lowered the labor consumption and reduced
363 arbitrariness.

364 Washing of asphaltene fraction in Soxhlet for a fixed amount of time eliminates the
365 necessity of setting arbitrary end time of washing. Arbitrariness was evaluated on the basis
366 of the precision of end points. In case of B1 and ASTM D3279 procedures end points are
367 quantitative whereas in ASTM D4124 it is qualitative (color of effluent). In ASTM D6560 the
368 washing step end point is measured in hours, however it is not fixed and only minimal time of
369 washing is given.

370

371 *Scaling up/automation*

372 Table 5 presents the results of scaling up possibility evaluation. To estimate scaling
373 up difficulty, the isolation process was divided into three parts: precipitation, filtration and
374 washing. To every stage two numbers were ascribed: one representing its significance
375 (wage) and second one describing difficulty of scaling up this stage. Difficulty was multiplied
376 by significance of considered step and sum of those multiplications was treated as scaling up
377 possibility parameter. Table 6 presents scale which was used to determine overall scale up
378 possibility of the procedure.

379 Precipitation step was considered as having the lowest significance for the
380 differentiation of the procedures because in every procedure it is conducted in the same way
381 and only volume of a solvent differs. This difference was used to determine difficulty of
382 scaling up. The bigger the feedstock to solvent ratio the bigger the vessel needed for
383 precipitation step.

384 When evaluating filtration step, time and power consumption were taken under
385 consideration. In case of ASTM D4124 significant problems with filtration resulting in



386 extended filtration time were discussed above. Additionally in ASTM D4124 and D3279
387 procedures vacuum is used for filtration which increases power consumption. Those remarks
388 are also true for washing step.

389 Due to the availability of wide range of Soxhlet dimensions, proposed procedure can
390 be easily scaled up, from laboratory scale to automated. Continuous washing with hot
391 solvent is also easier to implement on a process scale, than filtration through sub micrometer
392 filters. Moreover, in B1 procedure after filtration asphaltenes remain in thimble in which they
393 are washed and it should be easy to make it “one-pot” process. Additionally in B1 procedure
394 asphaltenes are not dissolved in toluene after washing with n-heptane as in ASTM D6560
395 and there is no need for evaporation to reprecipitate asphaltenes.

396

397 *Safety*

398 Conducting purification step in Soxhlet extractor reduces risk to safety and health. In
399 ASTM D4124 procedure washing with hot solvent is done manually and redissolving of
400 asphaltene fraction in hot n-heptane takes place in an open beaker. The lack of proper
401 attention can lead to overheating of the mixture, which may result in bumping, thus
402 representing a hazard.

403

404 **4. Conclusion**

405 The procedures of asphaltene fraction isolation developed and tested in this paper
406 provided higher purity of isolated fractions (containing less resins) and are characterized by
407 improved reproducibility and precision comparing to standard test method, which is
408 corroborated by the RSD% values.

409 Implementation of filtration through cellulose thimble and washing off isolated fraction
410 in Soxhlet extractor is less laborious, less arbitrariness and easy to scale-up. This simplicity
411 makes the scale-up easier which in connection with smaller solvent consumption per 1g of
412 feedstock can lead to obtaining higher quantities of asphaltene fraction, which may be

413 especially interesting for researchers working on characterization of asphaltenes e.g.
414 structural analysis and further if kilograms of asphaltenes are needed for different studies. In
415 this field particularly important are studies on bitumen properties related to asphaltene
416 content and their physico-chemical character.

417 As abovementioned, asphaltenes are currently under investigation in terms of their
418 sorption properties and employing them in separation techniques (Boczkaj et al., 2016,
419 2015). Such sorbents can be used in process scale separations or as a stationary phase for
420 gas chromatography. In this case further scaling-up will be needed and previously mentioned
421 advantages of proposed procedures can be crucial for isolating large quantities of this
422 material. Furthermore, in process scale isolation, washing step can be based on the same
423 principle as in Soxhlet extractor (recirculation of the hot solvent) and in turn will result in cost
424 reduction of this step.

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428 5/13/NCBR/2014.

429 **REFERENCES**

430 Aguiar, J.I.S., Mansur, C.R.E., 2015. Study of the interaction between asphaltenes and
431 resins by microcalorimetry and ultraviolet-visible spectroscopy. *Fuel* 140, 462–469.

432 Akbarzadeh, K., Hammami, A., Kharrat, A., Zhang, D., Allenson, S., Creek, J., Kabir, S.,
433 Jamaluddin, A., Marshall, A.G., Rodgers, R.P., Mullins, O.C., Solbakken, T., 2007.
434 Asphaltenes—problematic but rich in potential. *Oilf. Rev.* 22–43.

435 Ali, L.H., Al-Ghannam, K.A., 1981. Investigations into asphaltenes in heavy crude oils. I.
436 Effect of temperature on precipitation by alkane solvents. *Fuel* 60, 1043–1046.

437 Almehaideb, R.A., 2004. Asphaltene precipitation and deposition in the near wellbore region:
438 A modeling approach. *J. Pet. Sci. Eng.* 42, 157–170.

- 439 Andersen, S.I., 1995. Effect of precipitation temperature on the composition of n-heptane
440 asphaltenes Part 2. *Fuel Sci. Technol. Int.* 13, 579–604.
- 441 Andersen, S.I., 1994. Effect of precipitaiton temperature on the composition of n-heptane
442 asphaltenes. *Fuel Sci. Technol. Int.* 12, 51–74.
- 443 Andersen, S.I., Birdi, K.S., 1990. Influence of temperature and solvent on the precipitation of
444 asphaltenes. *Fuel Sci. Technol. Int.* 8, 593–615.
- 445 Andersen, S.I., Keul, A., Stenby, E., 1997. Variation in composition of subfractions of
446 petroleum asphaltenes. *Pet. Sci. Technol.* 15, 611–645.
- 447 Andersen, S.I., Lindeloff, N., Stenby, E.H., 1998. Investigation of asphaltene precipitation at
448 elevated temperature. *Pet. Sci. Technol.* 16, 323–334.
- 449 Andersen, S.I., Speight, J.G., 2001. Petroleum resins: separation, character, and role in
450 petroleum. *Pet. Sci. Technol.* 19, 1–34.
- 451 Andersen, S.I., Stenby, E.H., 1996. Thermodynamics o asphaltene precipitation and
452 dissolution investigation of temperature and solvent effects. *Fuel Sci. Technol. Int.* 14,
453 261–287.
- 454 ASTM D2007, 2003. Standard test method for characteristic groups in rubber extender and
455 processing oils and other petroleum – derived oils by the clay – gel absorption
456 chromatographic method.
- 457 ASTM D3279, 2001. Standard test method for n-heptane insolubles.
- 458 ASTM D4124, 2001. Standard test method for separation of asphalt into four fractions.
- 459 ASTM D6560, 2000. Standard test method for determination of asphaltenes (heptane
460 insolubles) in crude petroleum and petroleum products.
- 461 Badre, S., Carla Goncalves, C., Norinaga, K., Gustavson, G., Mullins, O.C., 2006. Molecular
462 size and weight of asphaltene and asphaltene solubility fractions from coals, crude oils

- 463 and bitumen. *Fuel* 85, 1–11.
- 464 Boczkaj, G., Kamiński, M., Momotko, M., Chruszczyk, D., 2015. Sorbent, kolumna sorpcyjna
465 lub chromatograficzna: sposób wykonania tych kolumn oraz sposób ich wykorzystania.
466 P.412584.
- 467 Boczkaj, G., Momotko, M., Chruszczyk, D., Przyjazny, A., Kamiński, M., 2016. Novel
468 stationary phases based on asphaltenes for gas chromatography. *J. Sep. Sci.* 39,
469 2527–2536.
- 470 Derakhshesh, M., Bergmann, A., Gray, M.R., 2013. Occlusion of polyaromatic compounds in
471 asphaltene precipitates suggests porous nanoaggregates. *Energy & Fuels* 27, 1748–
472 1751.
- 473 Ferris, S.W., Black, E.P., Clelland, J.B., 1967. Aromatic structure in asphalt fractions. *Ind.*
474 *Eng. Chem. Prod. Res. Dev.* 6, 127–132.
- 475 Groenzin, H., Mullins, O.C., 2000. Molecular size and structure of asphaltenes from various
476 sources. *Energy Fuels* 14, 677–684.
- 477 H. Alboudwarej, J. Beck, W. Y. Svrcek, A., Yarranton, H.W., Akbarzadeh, K., 2002.
478 Sensitivity of asphaltene properties to separation techniques. *Energy Fuels* 16, 462–
479 469.
- 480 Hu, Y.-F., Guo, T.-M., 2001. Effect of temperature and molecular weight of n-alkane
481 precipitants on asphaltene precipitation. *Fluid Phase Equilib.* 192, 13–25.
- 482 Hubbard, R.L., Stanfield, K.E., 1948. Determination of asphaltenes, oils, and resins in
483 asphalt. *Anal. Chem.* 20, 460–465.
- 484 Idris, M., Okoro, L.N., 2013. The effects of asphaltenes on petroleum processing. *Eur. Chem.*
485 *Bull.* 2, 393–396.
- 486 Jiang, C., Larter, S.R., Noke, K.J., Snowdon, L.R., 2008. TLC-FID (Iatroscan) analysis of
487 heavy oil and tar sand samples. *Org. Geochem.* 39, 1210–1214.



- 488 Kleinschmidt, L.R., 1955. Chromatographic method for the fractionation of asphalt into
489 distinctive groups of components. *J. Res. Natl. Bur. Stand.* (1934). 54, 163–166.
- 490 Kokal, S.L., Sayegh, S.G., 1995. Asphaltenes: the cholesterol of petroleum, in: *SPE Middle*
491 *East Oil Show*. p. paper SPE 29787.
- 492 Koots, J.A., Speight, J.G., 1975. Relation of petroleum resins to asphaltenes. *Fuel* 54, 179–
493 184.
- 494 León, O., Contreras, E., Rogel, E., Dambakli, G., Acevedo, S., Carbognani, L., Espidel, J.,
495 2002. Adsorption of native resins on asphaltene particles: a correlation between
496 adsorption and activity. *Langmuir* 18, 5106–5112.
- 497 Leyva, C., Ancheyta, J., Berrueco, C., Millán, M., 2013. Chemical characterization of
498 asphaltenes from various crude oils. *Fuel Process. Technol.* 106, 734–738.
- 499 Liao, Z., Geng, A., Graciaa, A., Creux, P., Chrostowska, A., Zhang, Y., 2006. Different
500 adsorption/occlusion properties of asphaltenes associated with their secondary
501 evolution processes in oil reservoirs. *Energy Fuels* 20, 1131–1136.
- 502 Liao, Z., Zhou, H., Graciaa, A., Chrostowska, A., Creux, P., Geng, A., 2005.
503 Adsorption/occlusion characteristics of asphaltenes: some implication for asphaltene
504 structural features. *Energy Fuels* 19, 180–186.
- 505 Linton, L.A., 1894. On the technical analysis of asphaltum. *J. Am. Chem. Soc.* 16, 809–822.
- 506 Maqbool, T., Srikiratiwong, P., Fogler, H.S., 2011. Effect of temperature on the precipitation
507 kinetics of asphaltenes. *Energy and Fuels* 25, 694–700.
- 508 Marcusson, J., 1911. Chemische Zusammensetzung und Unterscheidung der natürlichen un
509 kunstlichen Asphalte. *Chem. Rev. Fett- Harz-Ind.* 19, 166–171.
- 510 Mitchell, D.L., Speight, J.G., 1973. The Solubility of Aspahtlenes in hydrocarbon solvents.
511 *Energy Fuels* 52, 149–152.

- 512 Moschopedis, S.E., Speight, J.G., 1975. Oxidation of a bitumen. *Fuel* 54, 210–212.
- 513 Mullins, O.C., 2011. The asphaltenes. *Annu. Rev. Anal. Chem.* 4, 393–418.
- 514 Mullins, O.C., 2010. The modified yen model. *Energy Fuels* 24, 2179–2207.
- 515 Murgich, J., 2002. Intermolecular forces in aggregates of asphaltenes and resins. *Pet. Sci.*
516 *Technol.* 20, 983–997.
- 517 O'Donnell, G., Snider, L.T., Rietz, E.G., 1951. Separating asphalt into its chemical
518 constituents. *Anal. Chem.* 23, 894–898.
- 519 Parr, S.W., Mears, B., Weatherhead, D.L., 1909. The chemical examination of asphaltic
520 material. *J. Ind. Eng. Chem.* 1, 751–754.
- 521 Pineda, L.A., Trejo, F., Ancheyta, J., 2007. Correlation between properties of asphaltenes
522 and precipitation conditions. *Pet. Sci. Technol.* 25, 105–119.
- 523 Pomerantz, A.E., Wu, Q., Mullins, O.C., Zare, R.N., 2015. Laser-based mass spectrometric
524 assessment of asphaltene molecular weight, molecular architecture, and nanoaggregate
525 number. *Energy Fuels* 29, 2833–2842.
- 526 Ramirez-Jaramillo, E., Lira-Galeana, C., Manero, O., 2006. Modeling asphaltene deposition
527 in production pipelines. *Energy Fuels* 20, 1184–1196.
- 528 Rostler, F.S., Sternberg, H.W., 1949. Compounding rubber with petroleum products -
529 correlation of chemical characteristics with compounding properties and analysis of
530 petroleum products used as compounding ingredients in rubber. *Ind. Eng. Chem.* 41,
531 598–608.
- 532 Schuler, B., Meyer, G., Peña, D., Mullins, O.C., Gross, L., 2015. Unraveling the molecular
533 structures of asphaltenes by atomic force microscopy. *J. Am. Chem. Soc.* 137, 9870–
534 9876.
- 535 Sharma, B.K., Sarowha, S.L.S., Bhagat, S.D., Tiwari, R.K., Gupta, S.K., Venkataramani,



536 P.S., 1998. Hydrocarbon group type analysis of petroleum heavy fractions using the
537 TLC-FID technique. *Fresenius. J. Anal. Chem.* 360, 539–544.

538 Speight, J.G., 2004. Petroleum asphaltenes - Part 1: Asphaltenes, resins and the structure of
539 petroleum. *Oil Gas Sci. Technol.* 59, 467–477.

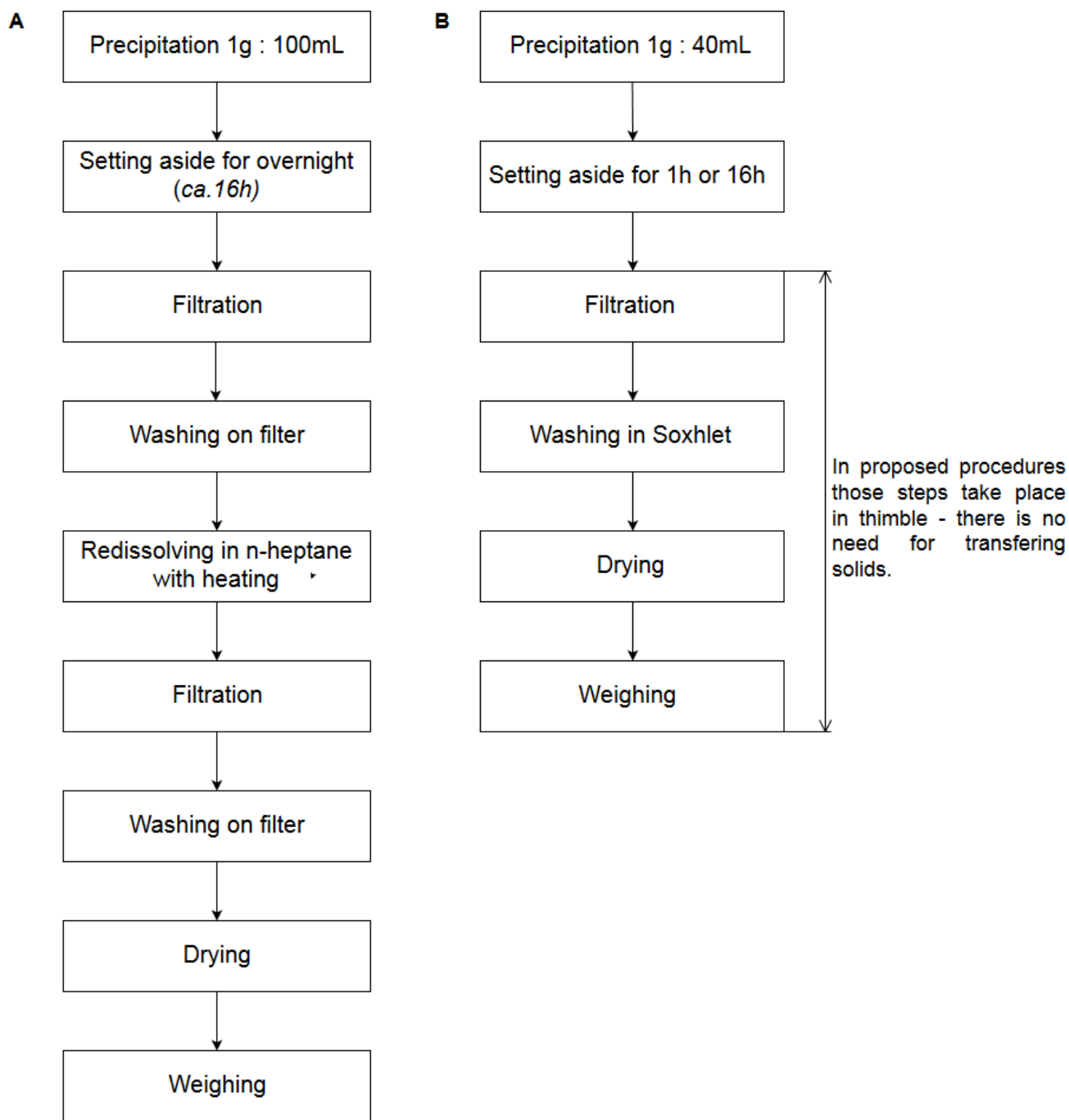
540 Speight, J.G., Long, R.B., Trowbridge, T.D., 1984. Factors influencing the separation of
541 asphaltenes from heavy petroleum feedstocks. *Fuel* 63, 616–620.

542 Strausz, O.P., Torres, M., Lown, E.M., Safarik, I., Murgich, J., 2006. Equipartitioning of
543 precipitant solubles between the solution phase and precipitated asphaltene in the
544 precipitation of asphaltene. *Energy Fuels* 20, 2013–2021.

545 Strieter, O.G., 1941. Method for determining the components of asphalts and crude oils. Part
546 J. Res. Natl. Bur. Stand. 26, 415-418.

547 Trejo, F., Centeno, G., Ancheyta, J., 2004. Precipitation, fractionation and characterization of
548 asphaltenes from heavy and light crude oils. *Fuel* 83, 2169–2175.

549



550

551 *Figure 1. Scheme of studied procedures for isolation of asphaltene fraction. (SINGLE COLUMN)*

552 *A) standard test method ASTM D4124. B) Proposed procedures. For two tested variants B1 and B16 the scheme*

553 *is the same, only time of setting aside changes (1h vs 16h).*

554

555
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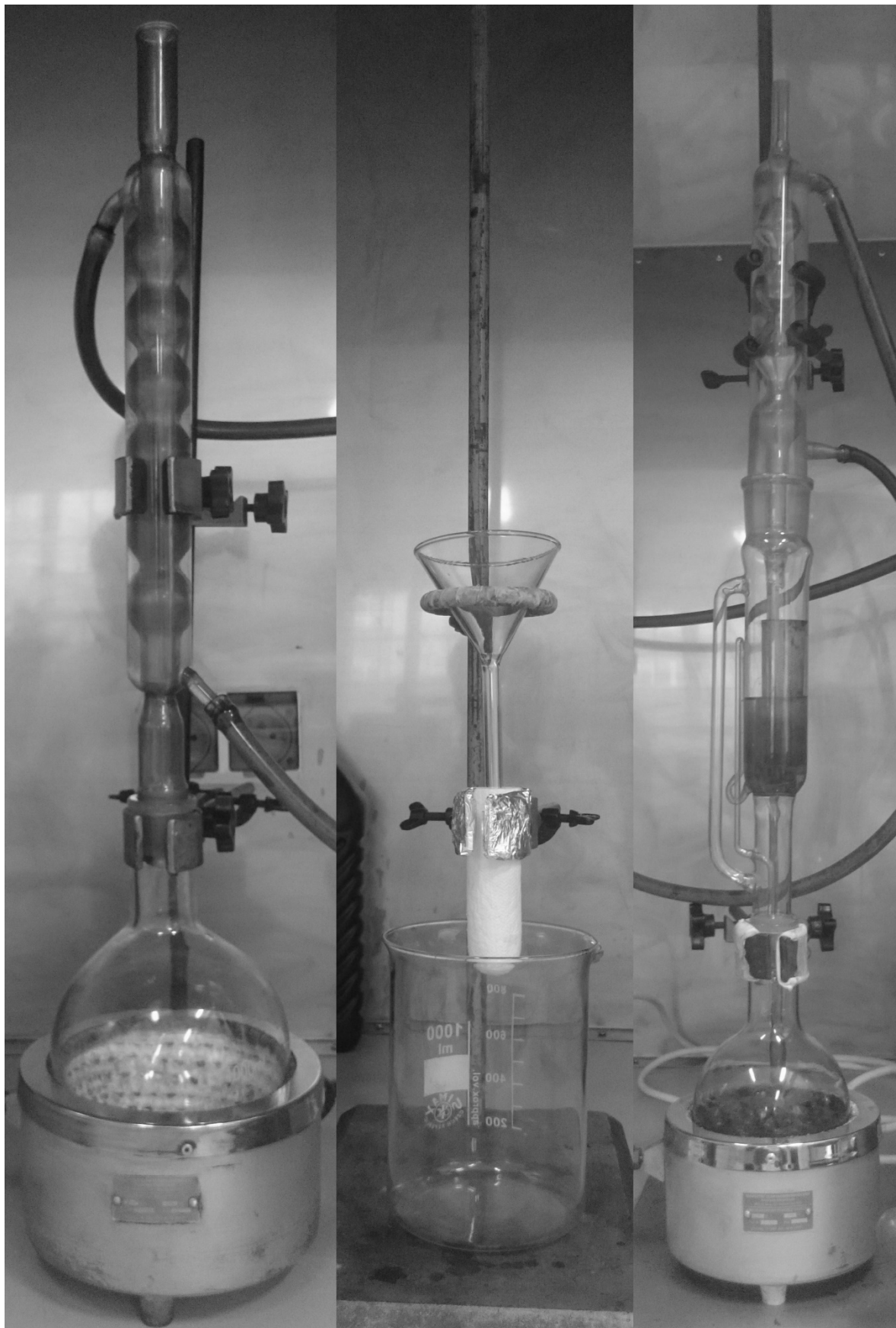
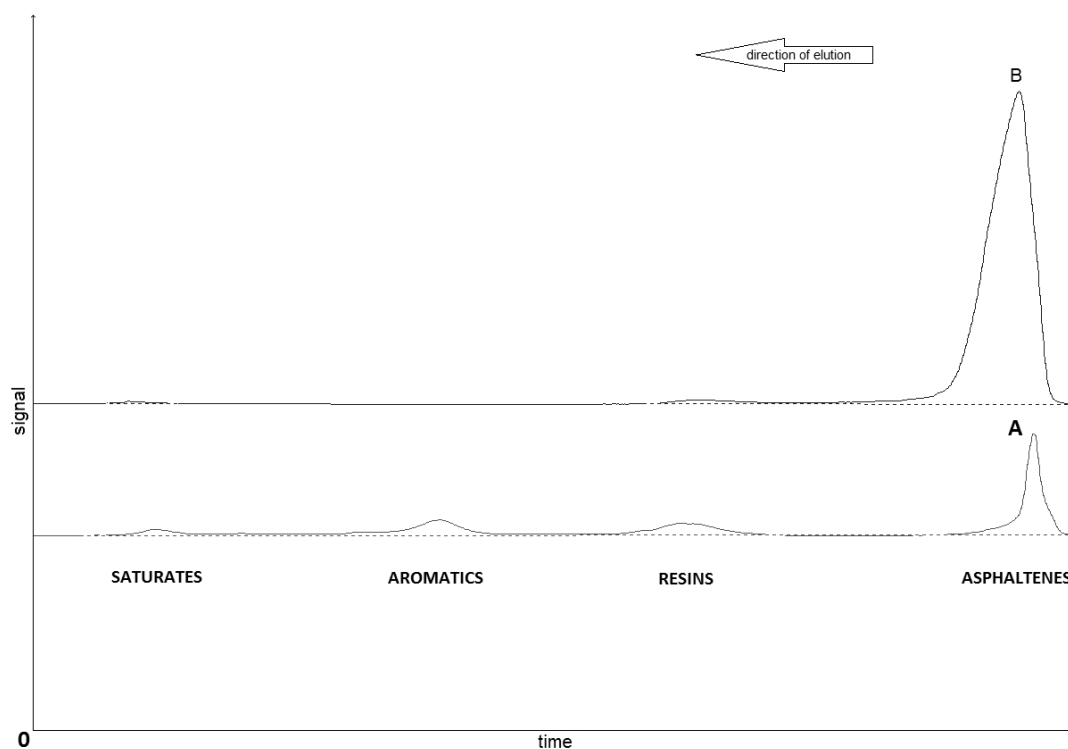


Figure 2. Experimental glassware setup. From left: precipitation set, filtration set, washing (Soxhlet) set. (**SINGLE COLUMN**)



558

559 *Figure 3. Exemplary TLC-FID chromatograms of SARA fractionation. (1.5-COLUMN)*560 *A) feedstock – bitumen 20/30 SDA and B) the asphaltene fraction isolated with tested B1 procedure.*

561

562 *Table 1. Comparison of asphaltenes isolation results obtained with tested procedures.(2-COLUMN)*

Method	ASTM D4124			B16			B1		
	Mean	STD	RSD%	Mean	STD	RSD%	Mean	STD	RSD%
Yield of asphaltene fraction [% m/m]	10.14	0.46	4.49	9.59	0.32	3.34	8.79	0.35	3.99
Asphaltene fraction purity[%]	95.80	0.30	0.31	96.49	0.47	0.49	97.39	0.76	0.78

563

564 *Table 2. Differences between results for tested procedures. (1.5-COLUMN)*

	ASTM D4124 – B16	ASTM D4124 – B1	B16 – B1
Yield of asphaltene fraction [% m/m]	0.55 ± 0.14	1.35 ± 0.11	0.80 ± 0.03

Asphaltenes content [%]	0.69 ± 0.17	1.59 ± 0.46	0.90 ± 0.29
--------------------------------	-------------	-------------	-------------

565

566 *Table 3. Comparison of variances and means for two sets of results. (1.5-COLUMN)*

	ASTM D4124 – B16	ASTM D4124 – B1	B16 – B1
	F-Snedecor		
	$F_{cr} (\alpha=0.05, f_1=f_2=2) = 19.00$		
	F		
Yield of asphaltene fraction [% m/m]	2.07	1.73	1.20
Asphaltenes content [%]	2.45	6.42	2.61
	t-Student		
	$t_{cr} (\alpha=0.05, f=n_1+n_2-2=4) = 2.776$		
	t		
Yield of asphaltene fraction [% m/m]	1.70	4.04	2.92
Asphaltenes content [%]	2.14	3.37	1.74

567

568 *Table 4. Comparison of procedures for isolation of asphaltene fraction. (2-COLUMN)*

	B1	ASTM D4124-01	ASTM D3279-07	ASTM D6560-00 (IP 143/01)
Time consumption	ca. 28h	ca. 20h	ca. 3h	ca. 10h
Solvent consumption	50 mL/g	ca. 150 mL/g	ca. 130 mL/g	heptane: ca. 50 mL/g toluene: ca. 10 mL/g
Washing	24h Soxhlet	on filter washing, until filtrate is colorless	on filter, 3 x 10mL	min. 1h reflux extractor
Laboriousness	+	-	+	--
Purity of asphaltene fraction	97.39 ± 0.76	95.80 ± 0.30	NA	NA

Scaling up/automation	easy	difficult	moderate	moderate
Safety	safe	hazardous steps	safe	safe
Arbitrariness	++	-	++	+

569

570 *Table 5. Collation of grades ascribed to isolation process stages describing its importance and difficulty of scaling*

571 *up. (2-COLUMN)*

Stage	Wage	B1		ASTM D4124-01		ASTM D3279-07		ASTM D6560-00	
		Difficulty	Mult.	Difficulty	Mult.	Difficulty	Mult.	Difficulty	Mult.
Precipitation	1	2	2	4	4	4	4	2	2
Filtration	2	2	4	5	10	3	6	3	6
Washing	3	2	6	4	12	3	9	4	12
Scaling up parameter			12		26		19		20

572

573 *Table 6. Scale used to determine the possibility of process scale up. (SINGLE COLUMN)*

Scaling up parameter	Scaling-up difficulty
≤ 15	easy
15-20	moderate
> 20	difficult

574